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TITLE: MULTI-DENTATE LATE TRANSITION METAL CATALYST
COMPLEXES AND POLYMERIZATION METHODS USING
THOSE COMPLEXES

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APPLICATION FOR UNITED STATES PATENT

MULTI-DENTATE LATE TRANSITION METAL CATALYST
COMPLEXES AND POLYMERIZATION METHODS USING THOSE
COMPLEXES

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MULTI-DENTATE LATE TRANSITION METAL CATALYST
COMPLEXES AND POLYMERIZATION METHODS USING THOSE
COMPLEXES

5 BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

[0001] The invention is directed towards multi-dentate late transition metal polymerization catalyst complexes and their use in forming polymers from olefins or polar monomers and copolymers from olefins and polar monomers.

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DESCRIPTION OF THE RELATED ART

[0002] Polymers and copolymers may be formed from olefinic monomers by using transition metal catalyst technology. Ziegler-Natta catalysts have been used for many years, while, in more recent years, metallocene catalysts have 15 been preferred in certain applications, since the polyolefins produced via metallocene catalysis often possess superior properties. The most well known metallocene technology employs catalysts containing early transition metal atoms, such as Ti and Zr.

[0003] Even though polyolefins formed by such metallocene catalysts possess 20 certain enhanced properties over polyolefins produced by conventional Ziegler-Natta catalysts, further improvements in properties such as wettability and adhesiveness may be possible. It is believed that including polar monomers in an olefinic polymer or copolymer would improve these, and possibly other, properties. Unfortunately, polar monomers tend to poison early transition metal 25 catalysts.

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[0004] Certain late transition metal complexes, such as those containing palladium and nickel, are more successful in incorporating certain polar monomers into polyolefins. However, most of these catalyst compositions are costly and produce highly branched polymers (e.g., 85-150 branches/1000 5 carbon atoms). Also, the functionalities are not in the chain, but at the ends of branches. Consequently, they are limited to polar monomer contents of about 15 mol% or less. Another disadvantage of these compositions is that they incorporate only a limited number of polar monomers, such as alkyl acrylates and vinyl ketones.

[0005] Recently, novel late transition organometallic catalysts have been made to address the aforementioned problems. More specifically, U.S. Patent No. 6,037,297 to Stibrany et al., incorporated by reference herein, details group 11 (Cu, Ag and Au; new IUPAC notation) metal-containing catalyst compositions having a pseudotetrahedral geometry that are useful in forming polymers and copolymers having hydrocarbyl polar functionality. Other 15 examples of group 11 metal-containing catalyst compositions are known. *See, e.g.*, WO 98/35996 and JPA 11-171915, both to Shibayama, et al. and both incorporated by reference herein.

[0006] However, there is still a need to explore other group 11 metal 20 complexes for use in polymerization processes. Ideally, these late transition metal complexes should be capable of forming olefinic polymers and copolymers containing polar monomers which are not highly branched, have polymer chain functionality and are capable of incorporating a wider variety of polar monomers.

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SUMMARY OF THE INVENTION

[0007] The instant invention provides a late transition metal complex which

can be used with an activating cocatalyst to produce polymers and copolymers. Further, the instant invention can be used to produce polymers and copolymers containing polar monomers. More specifically, the metal complex may be activated by a cocatalyst which is then used to polymerize olefins and 5 copolymerize olefins with polar monomers. Hence, the invention also provides methods for polymerizing olefins, as well as copolymers having polar monomers incorporated therein.

[0008] In one embodiment, the invention provides a composition having the formula $LMXZ_n$, wherein M is selected from the group consisting of Cu, Ag and 10 Au; X is selected from the group consisting of halide, hydride, triflate, acetate, borates, C_1 through C_{12} alkyl, C_1 through C_{12} alkoxy, C_3 through C_{12} cycloalkyl, C_3 through C_{12} cycloalkoxy, aryl, thiolate, nitrate, sulfate, nitrile, hydroxide and any other moiety into which a monomer can insert; Z is selected from the group consisting of halide, hydride, triflate, acetate, borate, C_1 through C_{12} alkyl, C_1 15 through C_{12} alkoxy, C_3 through C_{12} cycloalkyl, C_3 through C_{12} cycloalkoxy, aryl, thiolate, carbon monoxide, nitrate, nitrile, hydroxide, sulfate, olefins, water, any other neutral coordinating ligand and any other moiety into which a monomer can insert; n equals 0, 1 or 2; and L is a multi-dentate nitrogen-containing ligand.

[0009] In another embodiment, the invention is a catalyst composition 20 comprising the reaction product of a metal complex having the formula $LMXZ_n$, as defined above, and an activating cocatalyst. This embodiment of the invention is particularly useful in polymerization chemistry.

[0010] In yet another embodiment, the invention provides a method for using the composition to produce polymers and copolymers which contain polar 25 monomer units. The method includes contacting the monomers under polymerization conditions with a catalyst composition comprising a composition having the formula $LMXZ_n$, as defined above, and an activating cocatalyst. Optionally, an oxidizing agent may also be employed during this process.

[0011] In a further embodiment, the instant invention provides a novel olefin polymerization process based on the use of a group 11 transition metal complex having the formula MXZ_n , as defined above; a multi-dentate nitrogen-containing ligand L; and an activating cocatalyst, which are all contacted with monomers *in situ*. Unlike Atom Transfer Radical Polymerization (ATRP), the instant invention does not use an alkyl halide initiator, but instead uses a cocatalyst, and can be used to prepare homo- and co-polymers of aliphatic olefins. Further, unlike U.S. Patent No. 6,037,297, this embodiment of the invention teaches that the use of a preformed metal complex is not a prerequisite. More specifically, it is theorized that the metal complex may be formed *in situ* by adding the metal compound with a ligand at the same time cocatalyst is added. Hence, the advantages of the instant invention include an *in situ* method for forming an active catalyst composition which is a step-saving, cost-saving process.

[0012] These and other features, aspects and advantages of the present invention will become better understood with regard to the following description and appended claims.

DETAILED DESCRIPTION OF THE INVENTION

[0013] The invention relates to a novel metal complex which, when used with an activating cocatalyst, provides a novel catalyst composition. The invention also provides polymerization methods which utilize the catalyst composition. Generally speaking, the methods of the invention produce polymers and copolymers containing polar monomer groups. It should be appreciated by those skilled in the art that use of the general term "copolymers" includes terpolymers and other polymers having various combinations of monomer units.

[0014] In one embodiment, the invention comprises a composition comprising the formula $LMXZ_n$, wherein M is selected from the group

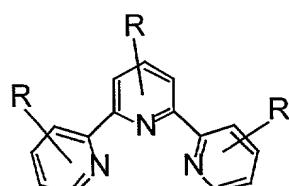
consisting of Cu, Ag and Au; X is selected from the group consisting of halide, hydride, triflate, acetate, borate, C₁ through C₁₂ alkyl, C₁ through C₁₂ alkoxy, C₃ through C₁₂ cycloalkyl, C₃ through C₁₂ cycloalkoxy, aryl, thiolate, nitrate, sulfate, nitrile, hydroxide and any other moiety into which a monomer can insert;

5 Z is selected from the group consisting of halide, hydride, triflate, acetate, borate, C₁ through C₁₂ alkyl, C₁ through C₁₂ alkoxy, C₃ through C₁₂ cycloalkyl, C₃ through C₁₂ cycloalkoxy, aryl, thiolate, carbon monoxide, nitrate, nitrile, hydroxide, sulfate, olefins, water, any other neutral coordinating ligand and any other moiety into which a monomer can insert; n equals 0, 1 or 2; and L is a

10 multi-dentate nitrogen-containing ligand. It should be appreciated by those skilled in the art that the term "multi-dentate" is meant to encompass tri-dentate, tetra-dentate, penta-dentate, hexa-dentate, etc., ligands. More specifically, there will be more than 2 coordinating nitrogen atoms in the ligand.

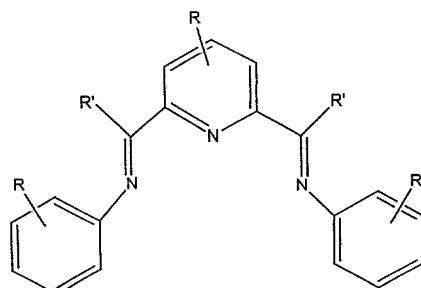
[0015] When the metal composition is reacted with an activating cocatalyst, such as methylaluminoxane ("MAO"), an activated catalyst composition is created. Thus, in another embodiment, the invention is an activated catalyst composition comprising the reaction product of: (a) a metal complex having the formula LMXZ_n, wherein M is selected from the group consisting of Cu, Ag and Au; X is selected from the group consisting of halide, hydride, triflate, acetate, borate, C₁ through C₁₂ alkyl, C₁ through C₁₂ alkoxy, C₃ through C₁₂ cycloalkyl, C₃ through C₁₂ cycloalkoxy, aryl, thiolate, nitrate, sulfate, nitrile, hydroxide and any other moiety into which a monomer can insert; Z is selected from the group consisting of halide, hydride, triflate, acetate, borate, C₁ through C₁₂ alkyl, C₁ through C₁₂ alkoxy, C₃ through C₁₂ cycloalkyl, C₃ through C₁₂ cycloalkoxy, aryl, thiolate, carbon monoxide, nitrate, nitrile, hydroxide, sulfate, olefins, water, a neutral coordinating ligand, and any other moiety into which a monomer can insert; n equals 0, 1 or 2; and L is a multi-dentate nitrogen-containing ligand; and (b) an activating cocatalyst.

[0016] In a preferred embodiment, L is a nitrogen-containing multi-dentate ligand selected from the group consisting of aromatic compounds, aliphatic compounds or a combination of aromatic and aliphatic compounds. The aromatic or aliphatic compounds can be acyclic compounds or they can be connected to form cyclic compounds. Examples of nitrogen-containing aromatic compounds include, but are not limited to, heterocycles, such as a substituted or unsubstituted 2,2':6'2"-terpyridine and a substituted or unsubstituted 2,6-diarylliminopyridine. Each sample heterocycle is shown below.



2,2':6'2"-terpyridine

[0017] For the terpyridine structure shown above, R is independently selected from the group consisting of hydrogen, C₁ to C₂₀ alkyl, C₄ to C₂₄ cycloalkyl and C₅ to C₃₀ aromatic groups which, optionally, contain heteroatoms. Although only three R groups are shown, there could be as many as 11 or more R groups, depending upon the size of the aromatic rings.

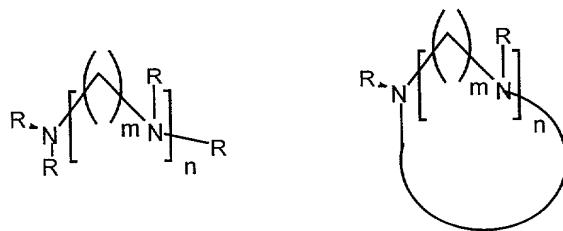


15 [2,6-bis(1-phenylimino)ethyl]pyridine

[0018] For the [2,6-bis(1-phenylimino)ethyl]pyridine structure shown above, R and R' are independently selected from the group consisting of hydrogen, C₁

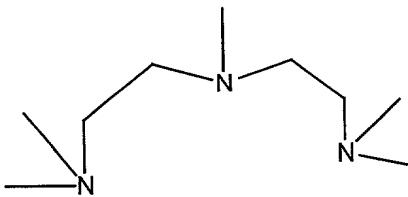
to C₂₀ alkyl, C₄ to C₂₄ cycloalkyl, and C₅ to C₃₀ aromatic groups which, optionally, contain heteroatoms. Although only three R groups and two R' groups are shown, there could be as many as 15 or more R and R' groups, depending upon the size of aromatic rings.

5 [0019] Similarly, examples of nitrogen-containing aliphatic compounds include, but are not limited to, substituted or unsubstituted diethylenetriamine or cyclic amine, as illustrated below:

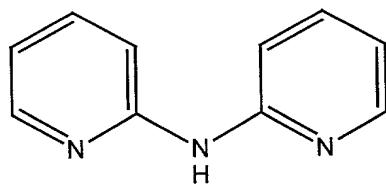


10 For the structures above, R is independently selected from the group consisting of hydrogen, C₁ to C₂₀ alkyl, cycloalkyl and aromatic groups which, optionally, contain heteroatoms. Furthermore, m is from 1 to 5, and n is from 0 to 5.

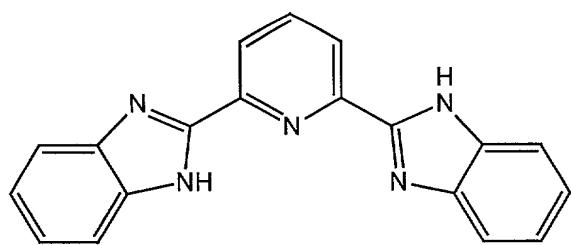
Specific examples of nitrogen-containing ligands include



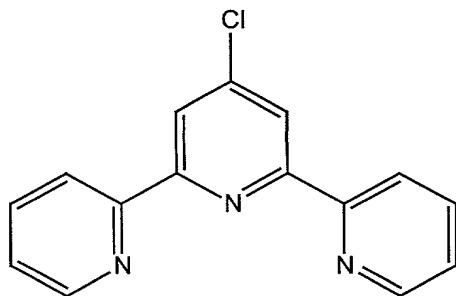
N,N,N',N",N"-pentamethyldiethylenetriamine



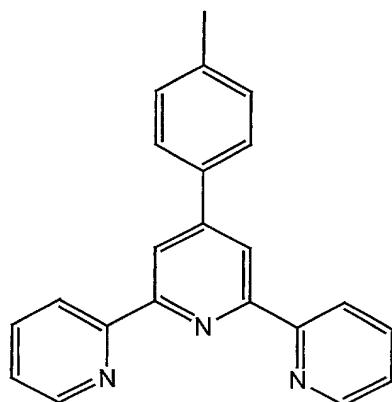
2,2'-dipyridylamine



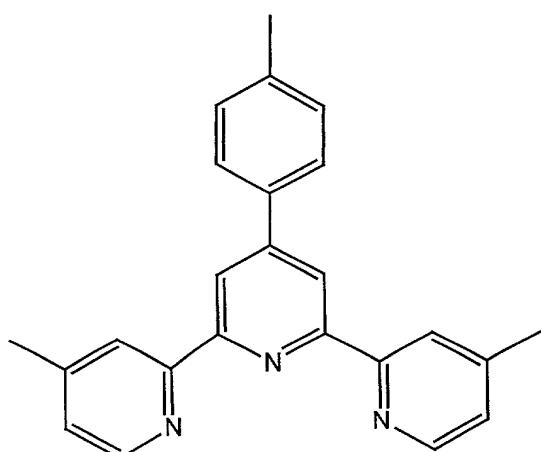
2,6-bis(1-hydrobenzimidazol-2-yl)pyridine



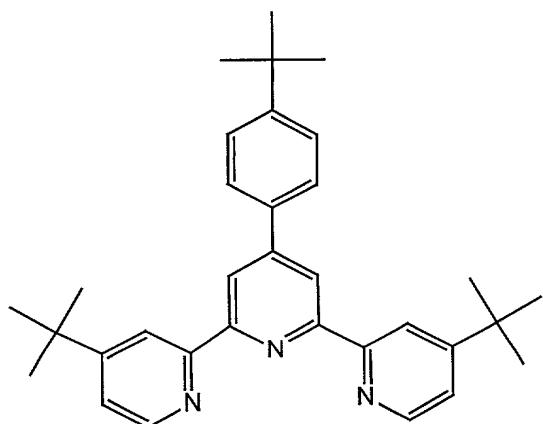
4-chloro-2,2':6',2"-terpyridine



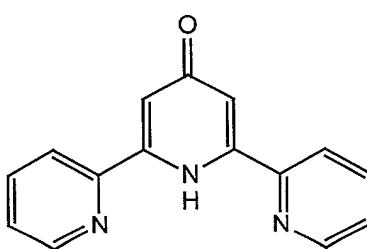
4'-(4-methylphenyl)-2,2':6',2"-terpyridine



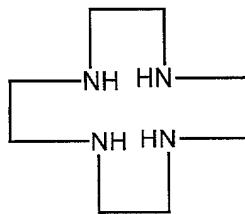
4,4'-dimethyl-4'-(4-methylphenyl)-2,2':6',2''-terpyridine



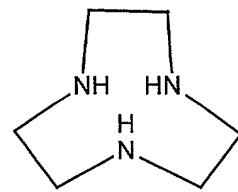
4,4',4"-tri-tert-butyl-2,2':6',2'-terpyridine



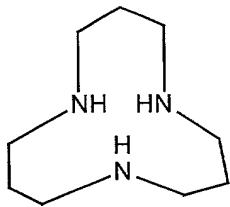
2,6-bis(2-pyridyl)-4(1H)-pyridone



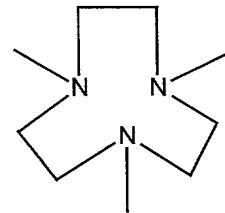
Cyclen (1,4,7,10-tetraazacyclododecane)



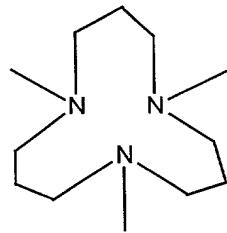
1,4,7-triazacyclononane



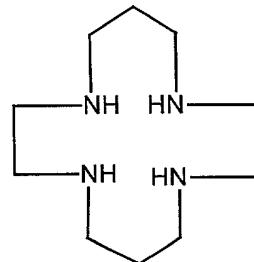
1,5,9-triazacyclododecane



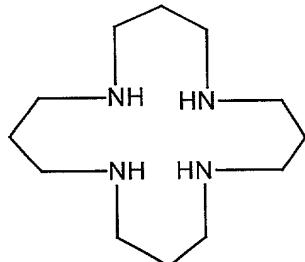
1,4,7-trimethyl-1,4,7-triazacyclononane



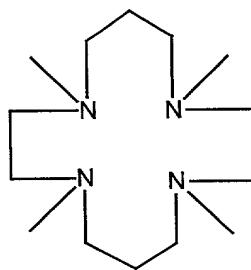
1,5,9-Trimethyl-1,5,9-triazacyclododecane



1,4,8,11-tetraazacyclotetradecane



1,5,9,13-tetraazacyclohexadecane



1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane

[0020] In yet another preferred embodiment, L may be a pyrazolyl borate compound, as taught in U.S. Patent No. 5,627,164 to Gorun, et al., incorporated by reference herein.

[0021] In a preferred embodiment, M is copper. Among the options for X, 5 halogens are preferred. Suitable non-halide options for X include, but are not limited to, triflate, trifluoroacetate, perfluorotetraphenyl borate, tetrafluoro borate, hydride, alkyl groups or any other moiety into which a monomer can insert, such as an atom, or group of atoms, covalently or ionically bonded to M.

[0022] For each occurrence of Z, each Z is preferably independently selected 10 from the group consisting of halogens, triflate, trifluoroacetate, perfluorotetraphenyl borate, tetrafluoro borate, hydride, alkyl, diethylether, tetrahydrofuran, acetonitrile, benzonitrile, dioxane, acetone, 2-butanone, phenylisocyanate, ethylene, carbon monoxide, 1-hexene and norbornene, or any other moiety into which a monomer can insert.

[0023] Advantageously, the catalysts of the present invention are not 15 poisoned by compounds containing hydrocarbyl polar functional groups when used in the formation of polymers and copolymers synthesized all or in part from olefinic monomers. As such, the catalysts of the present invention are useful in preparing polymers and copolymers formed from olefinic monomers, such as 20 polyethylene; polymers and copolymers formed from olefinic monomers containing hydrocarbyl polar functional groups, such as poly(methyl methacrylate); and copolymers derived from olefins and monomers containing hydrocarbyl polar functional groups, such as poly(ethylene-co-methyl methacrylate). One of skill in the art will know that the hydrocarbyl polar 25 functional groups mentioned above include ethers, esters, ketones, alcohols, and carboxylic acids, among others.

[0024] Examples of the activating cocatalysts used above include, but are not limited to, aluminum compounds containing an Al-O bond, such as the

alkylaluminoxanes, specifically methylaluminoxane ("MAO") and isobutyl modified methylaluminoxane; aluminum alkyls; aluminum halides; alkylaluminum halides; alkylaluminum alkoxides; alkylaluminum aryloxides; Lewis acids other than any of the foregoing list; and mixtures of the foregoing 5 can also be used in conjunction with alkylating agents, such as dimethyl magnesium, methyl magnesium chloride and methyl lithium. Examples of such Lewis acids are those compounds corresponding to the formula: R'''_3B , wherein R''' , independently each occurrence, is selected from hydrogen, silyl, hydrocarbyl, halohydrocarbyl, alkoxide, aryloxide, amide or combinations 10 thereof, said R''' having up to 30 non-hydrogen atoms.

[0025] It is to be appreciated by those skilled in the art that the above formula for the preferred Lewis acids represents an empirical formula, and that many Lewis acids exist as dimers or higher oligomers in solution or in the solid state. Other Lewis acids which are useful in the catalyst compositions of this invention 15 will be apparent to those skilled in the art.

[0026] Other examples of such cocatalysts include salts of group 13 element complexes (new IUPAC notation). These and other examples of suitable cocatalysts and their use in organometallic polymerization are discussed in U. S. Patent No. 5,198,401 and PCT patent documents WO 97/48736 and WO 20 1996/40805, all incorporated by reference herein.

[0027] Preferred activating cocatalysts include trimethylaluminum, triisobutylaluminum, methylaluminoxane, ethylaluminoxane, chlorodiethylaluminum, dichloroethylaluminum, triethylboron, trimethylboron, triphenylboron and halogenated, especially fluorinated, triphenyl boron 25 compounds.

[0028] The most highly preferred activating cocatalysts include, but are not limited to, triethylaluminum, methylaluminoxane, fluoro-substituted tetra-aryl borates, such as triphenylmethyl[tetrakis(pentafluorophenyl)borate], sodium

tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, and
dimethylanilinium[tetrakis(pentafluorophenyl)borate], and fluoro-substituted
triarylboranes, such as tris(4-fluorophenyl)boron, tris(2,4-difluorophenyl)boron,
tris(3,5-bis(trifluoromethyl)phenyl)boron, tris(pentafluorophenyl)boron,
5 (pentafluorophenyl-diphenyl)boron, and bis(pentafluorophenyl)phenylboron.
Such fluoro-substituted triarylboranes may be readily synthesized according to
techniques such as those disclosed in Marks, et al., J. Am. Chem. Soc., 113,
3623-3625 (1991), which is herein incorporated by reference.

[0029] Furthermore, the equivalent ratio of metal to activating cocatalyst is preferably in a range from 1:0.5 to 1: 10^4 , more preferably from 1:0.75 to 1: 10^3 . In most polymerization reactions, the equivalent ratio of catalyst:polymerizable compound employed is from 10^{-12} : 1 to 10^{-1} :1, more preferably from 10^{-9} :1 to 10^{-4} :1.

[0030] The catalyst can be utilized by forming the metal complex $LMXZ_n$, as defined above, and, where required, combining the activating cocatalyst with the metal complex in a diluent. Optionally, an oxidizing agent may also be utilized in conjunction with the cocatalyst. Oxidizing agents may include, but are not limited to, $NOBF_4$, 1,4-benzoquinone, tetrachloro-1,4-benzoquinone, $AgClO_4$, $Ag(C_6F_5)_4B$, ferricinium $(C_6F_5)_4B$, $(3, 5-(CF_3)_2-(C_6H_4)B)Cp_2Fe^+$, and $(3, 5-(CF_3)_2-(C_6H_4)B)Cp^*Fe^+$. The preparation may be conducted in the presence of one or more polymerizable monomers, if desired. Preferably, the catalysts are prepared at a temperature within the range from $-100^{\circ}C$ to $300^{\circ}C$, preferably from $0^{\circ}C$ to $250^{\circ}C$, and most preferably from $0^{\circ}C$ to $100^{\circ}C$. Suitable solvents include liquid or supercritical gases, such as CO_2 ; straight- and branched-chain hydrocarbons, such as isobutane, butane, pentane, hexane, heptane, octane, and mixtures thereof; cyclic and acyclic hydrocarbons, such as cyclohexane, cycloheptane, methylcyclohexane and methylcycloheptane; halogenated hydrocarbons, such as chlorobenzene, dichlorobenzene, and perfluorinated C_{2-10} alkanes; and aromatic and alkyl-substituted aromatic compounds, such as

benzene, toluene and xylene. Suitable solvents also include liquid olefins which may act as monomers or comonomers, including ethylene, propylene, butadiene, 1-hexene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1-octene, 1-decene, and 4-vinylcyclohexane (including all isomers alone or in mixtures). Other solvents 5 include anisole, methyl chloride, methylene chloride, chloroform, 2-pyrrolidone and N-methylpyrrolidone. Preferred solvents are aliphatic hydrocarbons and aromatic hydrocarbons, such as toluene.

[0031] Olefinic monomers useful in forming homopolymers and copolymers with the catalyst of the invention include, but are not limited to: (a) aliphatic 10 olefins; (b) olefins having a hydrocarbyl polar functionality; and (c) mixtures of (i) at least one olefin having a hydrocarbyl polar functional group and (ii) at least one aliphatic olefin. Olefinic monomers include ethylenically unsaturated monomers, nonconjugated dienes, oligomers, and higher molecular weight, vinyl-terminated macromers. Examples include C₂₋₂₀ olefins, vinylcyclohexane, 15 tetrafluoroethylene, and mixtures thereof. Preferred monomers include the C₂₋₁₀ α -olefins, especially ethylene, propylene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene, and 1-octene or mixtures of the same.

[0032] Monomers having hydrocarbyl polar functional groups useful in forming homopolymers and copolymers with the catalyst of the invention are 20 vinyl ether and C₁ to C₂₀ alkyl vinyl ethers, such as *n*-butyl vinyl ether; acrylates, such as C₁ to C₂₄ alkyl acrylates, preferably *t*-butyl acrylate and lauryl acrylate; and methacrylates, such as methyl methacrylate.

[0033] In another embodiment, the invention provides one method for 25 polymerizing olefinic monomers selected from the aforementioned group. The method of this embodiment comprises contacting the olefinic monomers under polymerization conditions with an activated catalyst compound comprising the reaction product of: (a) a metal complex having the formula LMXZ_n, as defined above; and (b) an activating cocatalyst. Furthermore, by controlling the

temperature, catalyst loading, ligand structure and residence time, product selectivity can be adjusted to produce individual polymers and copolymers with high selectivity.

[0034] A further embodiment comprises a method for polymerizing the aforementioned olefinic monomers *in situ*. This method includes contacting *in situ* under polymerization conditions compound MXZ_n, compound L, an activating cocatalyst, and one or more of the olefinic monomers. In this situation, the equivalent ratio of compound L to compound MXZ_n is preferably from 0.25:1 to 4:1, and more preferably from 0.5:1 to 2:1.

10 [0035] In general, the polymerization may be accomplished at conditions well known in the art for Ziegler-Natta or Kaminsky-Sinn type polymerization reactions, that is, temperatures from -100°C to 250°C, preferably from 0°C to 250°C, and pressures from atmospheric to 2000 atmospheres (200 Mpa).
15 Suitable polymerization conditions include those known to be useful for metallocene catalysts when activated by aluminum or boron compounds. Suspension, solution, slurry, gas phase or other process conditions may be employed, if desired. The catalysts may be supported, and such supported catalysts may be employed in the polymerizations of this invention. Preferred supports include alumina, silica, polymeric supports and meso-porous materials.

[0036] The polymerization typically will be conducted in the presence of a solvent. Suitable solvents include those previously described as useful in the preparation of the catalyst. Indeed, the polymerization may be conducted in the same solvent used in preparing the catalyst. Optionally, of course, the catalyst may be separately prepared in one solvent and used in another.

25 [0037] The polymerization will be conducted for a time sufficient to form the polymer, and the polymer is recovered by techniques well known in the art and illustrated in the following non-limiting examples which help to further

described the invention.

EXAMPLES

Example 1: Synthesis of (2,6-Bis-[1-(2,6-dimethylphenylimino)ethyl]-
5 pyridine)CuCl₂ ("I").

[0038] A 93 mg (0.56 mmol) quantity of CuCl₂•(H₂O)₂ mg, was dissolved in 10 mL anhydrous acetonitrile in a 100 mL Schlenk flask equipped with a stirbar and reflux condenser. Then, 2 mL of triethyl orthoformate was added and the clear green solution was heated to 84°C. Next, 202 mg (0.56 mmol) of 2,6-bis-

10 [1-(2,6-dimethylphenylimino)ethyl]-pyridine was dissolved in a mixture of 10 mL anhydrous acetonitrile and 0.6 mL toluene at 70°C and added to the copper chloride solution through the top of the condenser. The solution slowly became brown and, after 1 minute, a brown precipitate began to form. The mixture was stirred at 84°C for an additional 20 minutes and cooled to room temperature.

15 The brown precipitate was collected by filtration, rinsed with additional acetonitrile, and dried under vacuum (90 mg, 32% yield, FW 504.0 g/mol). IR (KBr): 3400 (w, residual O-H), 3080 (m), 2945 (m), 2909 (m), 1618 (m, Cu-Cl), 1565 (C=N), 1470 (s), 1373 (m), 1265 (s), 1223 (s), 1101 (w), 1034 (m), 814 (m), 770 (m), 744 (sh) cm⁻¹.

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Example 2: Preparation of (2,6-Bis-[1-(2,6-dimethylphenylimino)ethyl]-
pyridine)CuCl ("II").

[0039] A 67 mg (0.068 mmol) quantity of CuCl (rinsed with aqueous HCl and dried) was slurried in 20 mL anhydrous THF in a Schlenk flask equipped 25 with a stirbar and reflux condenser under argon. Next, 2 mL of triethyl orthoformate was added and the slurry was heated to 60°C. The 2,6-bis-[1-(2,6-

dimethylimino)ethyl]-pyridine (250 mg, 0.068 mmol) was dissolved in anhydrous THF and cannulated into the warm slurry. The CuCl began to dissolve and the mixture was allowed to reflux under argon for several hours, after which it had assumed a dark brown color. The solvent was removed by 5 cannula and the remaining solids rinsed with a small amount of anhydrous acetonitrile and dried under vacuum. Approximately 50 mg (16% yield, FW 468.5 g/mol) was recovered in the drybox as a brown powder. NMR (d_3 -acetonitrile): δ 8.29 (app. d, 2 H, Py-*m*), 8.27 (app. t, 1 H, Py-*p*), 7.14 (d, *J* = 7.6 Hz, 4 H, aniline *m*), 7.02 (t, *J* = 7.4 Hz, 2 H, aniline *p*), 2.27 (s, 6 H, N=CMe), 10 2.05 (s, 12 H, aniline Me). IR (KBr): 3450 (w), 3063 (w), 3017 (w), 2972 (m), 2917 (m), 1928 (w), 1620 (m), 1588 (s), 1468 (vs), 1368 (m), 1250 (s), 1206 (s), 1092 (m), 1036 (w), 988 (w), 810 (m), 770 (s) cm^{-1} .

Example 3: Preparation of (N,N,N',N",N"-

15 Pentamethyldiethylenetriamine)CuCl₂ ("III").

[0040] An 8.12 g (0.0952 mol) quantity of CuCl₂•(H₂O)₂ was dissolved in 250 mL ethanol in a 500 mL flask equipped with a stirbar and reflux condenser. Then, 50 mL of diethylene orthoformate was added, and the solution was stirred for 15 minutes. Next, a 7.5 g (FW 173.30, 0.0866 mol) quantity of 20 N,N,N',N",N"-pentamethyldiethylenetriamine was added. The mixture was refluxed for 30 minutes and cooled to room temperature. The flask was sealed and cooled in a refrigerator for crystallization to occur. The blue crystals were collected by filtration, rinsed with additional ethanol, and dried under a vacuum resulting in 2.13 g of the complex.

25

Example 4: Ethylene Polymerization

[0041] In an argon glovebox, 1.416 g of a 30 wt % methylaluminoxane solution in toluene (Albemarle, stored at -35°C, 425 mg MAO, 7.32 mmol) was weighed into a soap-washed and oven-dried 300 mL Parr glass liner. Then, 25 mL of chlorobenzene (distilled from CaH₂) and 25 mL of toluene (dried by passage over alumina and Q5 copper catalyst) were added followed by 45.6 mg (0.090 mmol) of **I**, the copper complex formed in Example 1. The liner was then placed into a 300 mL Hasteloy Parr reactor (soap-washed and oven-dried), which was quickly assembled, sealed and removed from the glove box. The reactor was heated to 80°C and the contents were stirred at approximately 350 rpm with an air-driven stirring shaft. After a quick nitrogen purge of the connected lines, the reactor was pressurized to 600 psi with ethylene (passed through drying columns of molecular sieves and Q5 copper catalyst). The reactor was sealed off from all gas lines and stirred at 80°C overnight, after which it was cooled to room temperature and vented. The contents were poured into a large excess (approx. 1 L) of 5% HCl in methanol. The white insoluble polymer was collected by filtration, rinsed with a small volume of additional methanol, and dried in a vacuum oven overnight at 75°C to yield 112 mg of the polymer. IR (KBr): 2917 (s), 2851 (s), 1472 (m), 729 (w), 719 (w) cm⁻¹. Melting point (DSC, 2nd heat): 134.9°C.

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Example 5: Polymerization of Ethylene

[0042] In an argon glovebox, 0.357 g of a 30 wt % methylaluminoxane solution in toluene (Albemarle, stored at -35°C, 107 mg MAO, 1.84 mmol) was weighed into a soap-washed and oven-dried 300 mL Hasteloy Parr reactor.

25 Then, 100 mL of toluene (dried by passage over alumina and Q5 copper catalyst) was added followed by 45.6 mg (0.090 mmol) of **I**, the copper complex formed in Example 1. The reactor was quickly assembled, sealed, removed from the glove box, and heated to 80°C, and its contents were stirred at approximately

350 rpm with an air-driven stirring shaft. After a quick nitrogen purge of the connected lines, the reactor was pressurized to 600 psi with ethylene (passed through drying columns of molecular sieves and Q5 copper catalyst). The reactor was sealed off from all gas lines and stirred for two days at 80°C, after 5 which it was cooled to room temperature and vented. The contents were poured into a large excess (approx. 1 L) of 5% HCl in methanol. The white insoluble polymer was collected by filtration, rinsed with a small volume of additional methanol, and dried in a vacuum oven overnight at 75°C to yield 226 mg of the polymer.

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Example 6: Polymerization of Ethylene

[0043] In an argon glovebox, 0.354 g of a 30 wt % methylaluminoxane solution in toluene (Albemarle, stored at -35°C, 106 mg MAO, 1.83 mmol) was weighed into a soap-washed and oven-dried 300 mL Parr glass liner. Next, 25 15 mL of chlorobenzene (distilled from CaH₂) and 25 mL of toluene (dried by passage over alumina and Q5 copper catalyst) were added, followed by 45.6 mg (0.090 mmol) of **I**, the copper complex from Example 1. The liner was placed into a 300 mL Hasteloy Parr reactor (soap-washed and oven-dried), which was quickly assembled, sealed and removed from the glove box. The reactor was 20 heated to 80°C and the contents were stirred at ca. 350 rpm with an air-driven stirring shaft. After a quick nitrogen purge of the connected lines, the reactor was pressurized to 600 psi with ethylene (passed through drying columns of molecular sieves and Q5 copper catalyst). The reactor was sealed off from all 25 gas lines and stirred overnight at 80°C, after which it was cooled to room temperature and vented. The contents were poured into a large excess (approx. 1 L) of 5% HCl in methanol. The white insoluble polymer was collected by filtration, rinsed with a small volume of additional methanol, and dried in a vacuum oven overnight at 75°C to yield 91 mg of the polymer.

Example 7: Polymerization of Ethylene

[0044] A glass-lined Parr reactor was loaded in an argon glove box with 100 mL of toluene and 10.53 g of 30 wt % MAO solution in toluene, and 0.0112 g of **III**, the copper complex formed in Example 3, was added. The Parr reactor was then sealed, placed in a fume hood and pressurized with 750 psig ethylene at 60°C for 24 hours. The reactor was cooled, vented and its contents poured into a solution of MeOH/HCl (300 mL MeOH/100 mL 10% HCl). The mixture was stirred for 24 hours to remove catalyst residues. The polymer was isolated by filtration and dried under vacuum at 60°C for 24 hours. The yield of the polyethylene was 120 mg. The IR spectrum (film) of the product showed the characteristic linear crystalline polyethylene doublet absorption at 719 and 729 cm^{-1} .

15 Example 8: Polymerization of *n*-Butyl Acrylate

[0045] In an argon glovebox, a 30 mL septum bottle was loaded with a 0.01 g (FW 309.75, 0.0322 mmol) quantity of **III**, the copper complex formed in Example 3, and 15 mL of toluene. A 0.77 g quantity of 30 wt % MAO solution in toluene was then added. The yellow solution turned colorless upon the MAO addition. Then, 5 g (FW 128.17, 0.039 mol) of *n*-butyl acrylate was added. The bottle was sealed in the glovebox and placed into a fume hood. The solution was stirred for 72 hours at 25°C. The viscous solution was added to a solution of MeOH/HCl (300 mL MeOH/100 mL 10% HCl solution to precipitate the polymer. The product was washed with water, then methanol, and dried in a vacuum oven for 24 hours at 60°C. The yield of the poly(*n*-butyl acrylate) was 3.26 g. The IR spectrum (film) of the product showed the characteristic polymer ester absorption peak at 1736 cm^{-1} . On polymerization, the monomeric ester

absorption peak shifts from 1728 cm^{-1} to the polymeric ester absorption at 1736 cm^{-1} . The characteristic double bond absorption peaks at 1637 and 812 cm^{-1} also disappear on polymerization. The GPC data (solvent: THF, polystyrene standard) gave a M_n of 119,600 and a M_w of 204,780. ^{13}C NMR (ppm, CDCl_3):

5 13.7 [s, - $\text{CH}_2\text{-CH}(\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)$ -], 19.1 [s, - $\text{CH}_2\text{-CH}(\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)$ -], 30.7 [s, - $\text{CH}_2\text{-CH}(\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)$ -], 34-37 [m, - $\text{CH}_2\text{CH}(\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)$ -], 41-42 [m, - $\text{CH}_2\text{-CH}(\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)$ -], 64.5 [s, - $\text{CH}_2\text{-CH}(\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)$ -], 174-175 [m, - $\text{CH}_2\text{-CH}(\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)$ -]. There were no resonances due to

10 olefin from the monomer.

Example 9: Copolymerization of Ethylene and *t*-Butyl Acrylate

[0046] A glass-lined Parr reactor was loaded in an argon glove box with 100 mL of toluene and 10.53 g of 30 wt % MAO solution in toluene. Then, a 0.0112 g quantity of **III**, the complex formed in Example 3, was added followed by 5 g of *tert*-butyl acrylate. The Parr reactor was sealed, placed in a fume hood and pressurized with 350 psig ethylene and heated to 60°C with stirring. The ethylene pressure was then increased to 700 psig and the reactor continued to stir for 18 hours at 60°C. The reactor was cooled, vented and its contents poured into a solution of MeOH/HCl (300 mL MeOH/100 mL 10% HCl). The mixture was stirred for 24 hours to remove catalyst residues. The polymer was isolated by filtration and dried under vacuum at 60°C for 24 hours. The yield of the copolymer was 310 mg. The IR spectrum of the product showed the characteristic ester absorption peak at 1728 cm^{-1} .

Example 10: Polymerization of Ethylene

[0047] In an argon glove box, a glass-lined Parr reactor was loaded with 120 mL of toluene and 2.84 g of 30 wt % MAO solution in toluene. A 10.6 mg quantity of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (FW 170.48, 6.218×10^{-2} mmol) was then added (Al/Cu ratio of 234) followed by a 10.4 mg quantity of $\text{N},\text{N},\text{N}',\text{N}'',\text{N}''$ -pentamethyldiethylenetriamine (FW 173.30, 6.00×10^{-2} mmol) ligand. The Parr reactor was sealed, placed in a fume hood and pressurized with 750 psig ethylene, and polymerized at 60°C for 20 hours. The reactor was cooled, vented and quenched with methanol. The polymer was soaked in a MeOH/HCl (300 mL MeOH/100 mL 10% HCl) mixture for 24 hours to remove catalyst residues. The polymer was isolated by filtration and dried under vacuum at 60°C for 24 hours. The yield of the polyethylene was 50 mg. The IR spectrum (film) of the product showed the characteristic linear crystalline polyethylene doublet absorption at 719 and 729 cm^{-1} .

Example 11: Polymerization of *t*-Butyl Acrylate

[0048] In an argon glovebox, a 30 mL septum bottle was loaded with a 0.0031 g quantity of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (FW 170.48, 0.02 mmol) and 15 mL of toluene. A 0.00315 g quantity of $\text{N},\text{N},\text{N}',\text{N}'',\text{N}''$ -pentamethyldiethylenetriamine ligand was then added, resulting in the formation of a yellow solution. Next, a 0.88 g quantity of 30 wt % MAO solution in toluene was added. The yellow solution turned colorless upon MAO addition. Then, 5 g of *t*-butyl acrylate (FW 128.17, 0.039 mol) was added. The bottle was sealed in the glove box and placed in a fume hood. The solution was heated at 60°C for 3 hours. The viscous solution was cooled to room temperature and was added to a MeOH/HCl (300 mL MeOH/100 mL 10% HCl) solution to precipitate the polymer. The

product was washed with water, then methanol, and dried in vacuum oven at 60°C for 24 hours. The yield of the poly(*t*-butyl acrylate) was 400 mg. The IR spectrum (film) of the product showed the characteristic ester peak at 1734 cm⁻¹.
13C NMR (ppm, CDCl₃): 27.7 (s, -CH₂-CH(COOC(CH₃)₃-), 35.9 and 37.1 (m, -
5 CH₂-CH(COOC(CH₃)₃), 42.3 (m, -CH₂-CH(COOC(CH₃)₃-), 79.6 (s, -CH₂-
CH(COOC(CH₃)₃-), 173.3 (s, -CH₂-CHCOOC(CH₃)₃-). There were no
resonances due to olefin from the monomer.

Example 12: Copolymerization of Ethylene and *t*-Butyl Acrylate

10 [0049] In an argon glove box, a 0.0062 g quantity of CuCl₂.2H₂O (FW 170.48, 0.04 mmol) and 100 mL of toluene were loaded into a glass-lined Parr reactor. Then, a 0.0068 g quantity of N,N,N',N'',N''-pentamethyldiethylenetriamine ligand was added, which cause the solution to turn yellow. Next, a 1.53 g quantity of 30 wt % MAO solution in toluene was
15 added. Then, a 5 g quantity of *t*-butyl acrylate (FW 128.17, 0.039 mol) was added. The Parr reactor was then sealed, placed in a fume hood, and pressurized with 750 psig ethylene, and polymerized at 60°C for 20 hours. The reactor was cooled, vented and quenched with methanol. The polymer was soaked in a MeOH/HCl mixture (300 mL MeOH/100 mL 10% HCl) for 24 hours to remove
20 catalyst residues. The polymer was isolated by filtration and dried under vacuum at 60°C for 24 hours. The yield of the product was 250 mg. ¹³C NMR spectra of the product showed EAE, EAA/AAE and AAA triads and a copolymer composition of 56% ethylene (E) and 46% acrylate (A).

Example 13: Polymerization of Ethylene

[0050] A glass-lined Parr reactor was loaded in an argon glove box with 120 mL of toluene and 2.84 g of a 30 wt % MAO solution in toluene. A 11.0 mg quantity of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (FW 170.48, 6.452×10^{-2} mmol) was then added (Al:Cu ratio of 227:1) followed by a 10.0 mg quantity of 1,4,7-trimethyl-1,4,7-triazacyclononane (FW 171.29, 5.84×10^{-2} mmol) ligand. The Parr reactor was then sealed, placed in a fume hood, and pressurized with 750 psig ethylene, and polymerized at 60°C for 16 hours. The reactor was cooled, vented and quenched with methanol. The polymer was soaked in a MeOH/HCl mixture (300 mL MeOH/100 mL 10% HCl) for 24 hours to remove catalyst residues. The polymer was isolated by filtration and dried under vacuum at 60°C for 24 hours. The yield of the polyethylene was 110 mg. The IR spectrum (film) of the product showed the characteristic linear crystalline polyethylene doublet absorption at 719 and 729 cm^{-1} .

Example 14: Polymerization of *n*-Butyl Acrylate

[0051] In an argon glovebox, a 30 mL septum bottle was loaded with a 0.0061 g quantity of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (FW 170.98, 3.57×10^{-2} mmol) and 15 mL of toluene. Then, a 0.0056 g quantity of 1,4,7-trimethyl-1,4,7-triazacyclononane (FW 171.29, 3.327×10^{-2} mmol) ligand was added, resulting in a yellow solution. A 0.77 g quantity of 30 wt % MAO solution in toluene was then added. The yellow solution turned colorless upon MAO addition. Next, a 5 g quantity of *n*-butyl acrylate (FW 128.17, 0.039 mol) was added. The bottle was sealed in the glove box and placed in a fume hood. The solution was stirred at 25°C for 72 hours. The viscous solution was added to a MeOH/HCl (300 mL MeOH/100 mL 10% HCl) solution to precipitate the polymer. The product was

washed with water, then methanol, and dried in a vacuum oven at 60°C for 24 hours. The yield of the poly(*n*-butyl acrylate) was 4.12 g. The IR spectrum (film) of the product showed the characteristic polymer ester absorption peak at 1736 cm⁻¹. After polymerization, the monomeric ester absorption peak shifted 5 from 1728 cm⁻¹ to the polymeric ester absorption at 1736 cm⁻¹. The characteristic double bond absorption peaks at 1637 cm⁻¹ and 812 cm⁻¹ also disappeared upon polymerization. The GPC data (solvent: THF, polystyrene standard) gave a M_n of 112,200 and a M_w of 160,700. ¹³C NMR (ppm, CDCl₃): 13.6 [s, -CH₂-CH(COOCH₂CH₂CH₂CH₃)-], 19.1 [s, -CH₂-CH 10 (COOCH₂CH₂CH₂CH₃)-], 30.7 [s, -CH₂-CH(COOCH₂CH₂CH₂CH₃)-], 34-37 [m, -CH₂CH(COOCH₂CH₂CH₂CH₃)-], 41-42 [m, -CH₂-CH(COOCH₂CH₂CH₂CH₃)-], 64.5 [s, -CH₂-CH(COOCH₂CH₂CH₂CH₃)-], 174-175 [m, -CH₂-CH(COOCH₂CH₂CH₂CH₃)-]. There were no resonances due to olefin from the monomer.

15

Example 15: Polymerization of *n*-Butyl Acrylate

[0052] In an argon glovebox, a 30 mL septum bottle was loaded with a 0.0061 g quantity of CuCl₂.2H₂O (FW 170.98, 0.0357 mmol) and 15 mL of toluene. Then, a 0.0130 g quantity of 4,4',4''-tri-*tert*-butyl-2,2':6',2'-terpyridine 20 (FW 401.60, 0.0324 mmol) ligand was added resulting in the formation of a yellow solution. A 0.77 g quantity of 30 wt % MAO solution in toluene was then added. The yellow solution turned colorless upon MAO addition. Next, 5 g of *n*-butyl acrylate (FW 128.17, 0.039 mol) was added. The bottle was sealed in the glove box and placed in a fume hood. The solution was stirred at 25°C for 72 hours. The viscous solution was added to a MeOH/HCl (300 mL MeOH/100 mL 10% HCl) solution to precipitate the polymer. The product was washed with water, then methanol, and dried in vacuum oven at 60°C for 24 hours. The yield 25 of the poly(*n*-butyl acrylate) was 3.12 g. The IR spectrum (film) of the product

showed the characteristic polymer ester absorption peak at 1736 cm⁻¹. On polymerization, the monomeric ester absorption peak shifted from 1728 cm⁻¹ to the polymeric ester absorption at 1736 cm⁻¹. The characteristic double bond absorption peaks at 1637 cm⁻¹ and 812 cm⁻¹ also disappeared upon 5 polymerization. The GPC data (solvent: THF, polystyrene standard) gave a M_n of 124,100 and a M_w of 214,600 ¹³C NMR (ppm, CDCl₃): 13.7 [s, -CH₂-CH(COOCH₂CH₂CH₂CH₃)-], 19.1 [s, -CH₂-CH(COOCH₂CH₂CH₂CH₃)-], 30.7 [s, -CH₂-CH(COOCH₂CH₂CH₂CH₃)-], 34-37 [m, -CH₂CH(COOCH₂CH₂CH₂CH₃)-], 41-42 [m, -CH₂-CH(COOCH₂CH₂CH₂CH₃)-], 64.5 [s, -CH₂-CH(COOCH₂CH₂CH₂CH₃)-], 174-175 [m, -CH₂-CH(COOCH₂CH₂CH₂CH₃)-].
10 There were no resonances due to olefin from the monomer.

[0053] The foregoing examples clearly demonstrate that the novel composition of the instant invention can be used as an effective polymerization 15 catalyst to make polymers and copolymers, including copolymers having polar functionality. More specifically, the examples show how polar monomers can be readily polymerized without poisoning the catalyst. Also, the chain, as opposed to the branches, contains a significant quantity of the polar monomers. Furthermore, the polymers formed are not highly branched. Additionally, the 20 examples show that the polymers formed have a high percent of polar monomer content (e.g., greater than about 15 mol%). Finally, there are a variety of polar monomers which may be incorporated into the olefinic polymer and copolymer products. These features overcome the disadvantages of most organometallic catalyst technology used today, as discussed above in the background section.